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Journal of Colloid and Interface Science 608 (2022) 1116–1125 Contents lists available at ScienceDirect Journal of Colloid and Interface Science journal homepage: www.elsevier.com/locate/jcis Suppressing photoinduced charge recombination at the BiVO4||NiOOH junction by sandwiching an oxygen vacancy layer for efficient photoelectrochemical water oxidation Yong Peng

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19**Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Renewable Energy Conversion and Storage Center (RECAST), College of Chemistry, Nankai University, Tianjin**, PR **China**

i Hubei Key Laboratory of Plasma Chemistry and Advanced Materials, School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430205, PR China graphical abstract article info Article history: Received 29 July 2021 Revised 11 October 2021 Accepted 12 October 2021 Available online 23 October 2021 Keywords: Photoelectrochemistry Surface engineering Oxygen vacancies abstract Nickel oxyhydroxide (NiOOH) is regarded as one of the promising cocatalysts to enhance the catalytic performance of photoanodes but suffers from serious interfacial charge-carrier recombination at the photoanode||NiOOH interface. In this work, surface-engineered BiVO4 photoanodes are fabricated by sandwiching an oxygen vacancy (Ovac) interlayer between BiVO4 and NiOOH. The surface Ovac interlayer is introduced on BiVO4 by a chemical reduction treatment using a mild reducing agent, sodium hypophosphite. The induced Ovac can alleviate the interfacial charge-carrier recombination at the BiVO4||NiOOH junction, resulting in efficient charge separation and transfer efficiencies, while an outer NiOOH layer is coated to prevent the Ovac layer from degradation. As a result, the as-prepared NiOOH-P-BiVO4 photoanode exhibits

37**a high photocurrent density of 3**.2 **mA cm?2 at 1.23 V vs. RHE under**

the irradiation

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https://doi.org/10.1016/j.jcis.2021.10.063 0021-9797/ Nickel oxyhydroxide of 100 mW/cm2 AM 1.5G simulated sunlight,

5**in comparison to** those **of** bare **BiVO4**, P-**BiVO4, and** NiOOH- **BiVO4**

photoanodes (1.1, 2.1 and 2.3 mA cm?2, respectively). In addition to the superior photoactivity, the 5-h amperometric measurements illustrate improved stability of the surface-engineered NiOOH-P-BiVO4 photoanode. Our work showcases the feasibility of combining cocatalysts with Ovac, for improved photoactivity and stability of photoelectrodes. 1. Introduction Bismuth vanadate (

6**BiVO4) is one of the** potential **candidates for photoelectrochemical (PEC) water**

splitting to produce hydrogen fuel in the future. The photoanode is endowed with a suitable bandgap structure (the bandgap of 2.4 eV and conduction band edge of 0.02 V vs. RHE for hydrogen production) and moderate charge carrier lifetime [1]. Despite this, unacceptable charge carrier

24**recombination and poor water oxidation kinetics** have significantly impaired **the** PEC **performance of**

this photoanode [2]. To tackle the issue, versatile strategies including doping engineering [3], mor- phology engineering [4], heterostructure engineering [5], and sur- face

5**modification of oxygen evolution catalysts (OECs**

) [6], have been

32**employed to** promote **the PEC performance of** BiVO4 **photoanodes. In** general, **the**

overlayer of OECs has been recognized as a useful strategy to accelerate water oxidation reaction and alleviate bulk electron-hole pair recombination. Numerous OECs such as metal phosphates (e.g., CoPi) [7], metal phosphides (CoP) [8], metal oxi- des (IrO2 and CoOx) [9], and metal (oxy)hydroxides (Ni(OH)2 and NiOOH) [9c,10], have been designed for improving the photoactiv- ity of BiVO4 photoelectrodes. Among these catalysts, metal oxyhy- droxides such as iron oxyhydroxide (FeOOH) and nickel oxyhydroxide (NiOOH) have gained much attention because of their prominent catalytic activity, earth abundance, and environ- mental friendliness [11]. Notably, the modification of NiOOH as an OEC on BiVO4 photoanodes enables a lower onset potential in comparison to FeOOH, which indicates an exceedingly active water oxidation process [6a]. Despite these benefits, considerable interfa- cial recombination of electron-hole pairs at the BiVO4||NiOOH interface has significantly jeopardized its photoactivity [6a], which raises concerns about applying NiOOH for practical uses. To eliminate interfacial charge carrier recombination, introduc- ing an oxygen vacancies (Ovac) layer between the BiVO4 photoan- ode and the NiOOH overlayer may be one of the effective strategies [12]. This is because Ovac has the opportunity to modify the electronic structure and create inter-band states in the forbid- den band of BiVO4, resulting in both enhanced conductivity and promoted charge separation [12–13]. In the meantime, the over- laid cocatalysts may also

36**serve as a protective layer**, preventing **the** degradation **of the**

Ovac layer which is not stable in a highly oxi- dizing environment [12]. In view of these aspects, we propose that interfacial charge recombination may be suppressed with a rational sandwiched Ovac layer between BiVO4 photoanodes and NiOOH cocatalysts. Herein, an interfacial Ovac layer has been introduced to BiVO4 photoanodes by a chemical reduction treatment using a mild reducing agent, sodium hypophosphite. The induced Ovac inter- layer can decrease interfacial charge carrier recombination, as indi- cated by the charge separation and transfer efficiencies, while the outer NiOOH layer as active sites for the oxidation of water is loaded to simultaneously prevent the Ovac interlayer from degrada- tion. As a result of the alleviation of the interfacial carrier recombi- nation and the acceleration of water oxidation reaction, the PEC performance of BiVO4 photoanodes can be considerably enhanced. In this work, we provide an effective and facile strategy to coordi- nate OECs and Ovac, leading to an improved photoactivity of metal oxide semiconductors. 2. Materials and methods 2.1. Fabrication of BiVO4, P-

2**BiVO4, NiOOH-BiVO4 and NiOOH**-P-**BiVO4**

films Bare BiVO4 films on FTO glass (6–9 X/sq) were synthesized using a reported electrodeposition method followed by the calcina- tion [6a,14]. The pH of 50 mL DI water was adjusted to 1.7 using 65% HNO3. Next,

15**3.32 g** of **KI and 0.97 g** of **Bi(NO3)3** 5H2O **were**

sub- sequently added and dissolved in the aqueous solution. The as- prepared

10**solution was mixed with 20 mL** of **0.23 M p- benzoquinone**

dissolved in ethanol, which was then used as an electrolyte.

35**FTO substrates** (1.**5 cm** 3.**0 cm**

) were cleaned by son- icating them

36**in acetone, ethanol, and** DI **water**, each **for 20 min. The**

cathodic deposition was then performed using a three-electrode system including the FTO glass as a

2**working electrode**, a **Pt** wire **as the counter electrode, and** an **Ag/AgCl (3 M) as the reference electrode**. During amperometric deposition, **the** potential **was** set **at ?0**.1 **V vs. Ag/AgCl, and** each electrodeposition lasted **for**

5 min to achieve a total charge of around 0.13C cm?2. The obtained BiOI films were calcined with 300 IL of

1**0.2 M VO(acac)2** in DMSO **at 450 °C for 2 h. The** as-obtained **BiVO4**

30**films were** treated **in 1 M NaOH for 30 min to remove V2O5**

. To induce Ovac into BiVO4, the bare BiVO4 photoanodes were placed into 0.5 M sodium hypophosphite (Na2H2PO2 H2O) and heated at 90 °C for 6 h in an oven. After the treatment, the as- obtained hypophosphite-treated BiVO4 (labeled as P-BiVO4)

6**was rinsed with** DI **water and dried** with compressed **air. The**

optimiza- tion processes for the concentration of hypophosphite, heating temperature, and duration are shown in Figure S1 (Supplementary Information, SI). To facilitate charge transfer, the NiOOH cocatalyst layer was deposited on the BiVO4 and P-BiVO4 photoanodes using a pH-adjusting method [15]. Specifically, after immersing the pho- toanodes into 10 mM Ni(NO3)2 6H2O for 15 min, the pH of the solu- tion was adjusted to be around 8.0 using 2 M NaOH. After that, the solution was remained still for 45 min to deposit NiOOH on the photoanodes. Finally, the obtained NiOOH-coated photoanodes (named NiOOH-BiVO4 and NiOOH-P-BiVO4, respectively) were identically rinsed and dried. 2.2. Material characterizations The surface morphology was observed by Zeiss EVO MA10 scan- ning electron microscope (SEM) and FEI Tecnai F20 field-emission transmission electron microscope (TEM). The elemental mapping was collected by the FEI Tecnai F20

11**equipped with an energy- dispersive X-ray** spectroscope (**EDS**) under STEM mode. **X-ray diffraction** (XRD) **patterns**

were measured with PANalytical X’Pert3 X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was performed by the Thermo Scientific K-Alpha+ XPS spectrometer.

23**All binding energies were calibrated with respect to C** 1 s **peak at 284**.8 **eV**

.

23**Electron paramagnetic resonance (EPR) spectra were** measured with **a Bruker** A300 **spectrometer**

.

40**Raman spectra were** collected **by a** HORIBA iHR320 **Raman**

microscope with a 514-nm laser. UV–visible absorption spectra were measured using Shi- madzu UV-3600 spectrophotometer with an integrated sphere. Photoluminescence (PL) spectra were analyzed using Shimadzu RF-5301PC spectrometer. Time-resolved photoluminescence (TRPL) spectra were measured by the PicoQuant Fluo Time 200 spectrometer coupled with a TimeHarp 260 time-correlated single-photon counting (TCSPC) system. 2.3. Electrochemical and photoelectrochemical characterizations A three-electrode system was used for electrochemical and photoelectrochemical measurements using a CHI660 workstation (Chenhua, Shanghai). The as-obtained films

17**were used as working** electrodes, while the **counter electrode**

21**and the** reference **electrode were Pt** wire **and Ag/AgCl (3 M**), respectively. The photoanodes **were** back-side illuminated by

6**a 300 W xenon lamp** equipped **with an AM 1**.5G **filter and the optical power was calibrated to 100 mW** cm?2. A **0.5 M** Na2SO4 aqueous **solution (pH**

6.6)

25**was used as the electrolyte** during **the** measurements. The **potential versus Ag/AgCl was converted to** potential versus reversible **hydrogen electrode (RHE**) based on **the** following **equation: ERHE ¼ EAg=AgCl þ**

EAg=

29**AgCl þ 0:059 pH where** ERHE **is the converted potential versus RHE, E>Ag/AgCl is the** standard electrode **potential** of **Ag/AgCl**

electrode against the stan- dard hydrogen electrode and equals to 0.210

38**V at 25 °C, and EAg/AgCl is the experimentally measured potential versus Ag/AgCl electrode**

.

15**Linear sweep voltammetry (LSV**) technique **was** carried out **from ?0**.7 **to 1**.0 **V vs**. Ag/AgCl **at a** scan **rate of** 10 **mV s?1 under** the **dark**

or light condition to obtain current–potential (J-V) curves. Electrochemical impedance spectra (EIS) were collected at an imposed potential of 0.63 V vs. Ag/AgCl (equal to 1.23

3**V vs. RHE) with** frequencies **ranging from** 105 **to 0**.5 **Hz**

and an amplitude volt- age of 10 mV under illumination. The resultant EIS spectra were fit- ted using the Zview software. For transient photocurrent measurements, also called amperometric i-t tests, BiVO4 films were imposed

17**with a bias potential of 0**.63 **V vs. Ag/AgCl**

under chopped illumination (light 50 s/dark 50 s). For testing the stability of BiVO4 films, the illumination lasts for 5 h at the same bias potential. Mott-Schottky (M?S) analysis

34**was performed at a frequency of** 1000 Hz at **an amplitude of** 10 **mV from ? 0**.6 V **to 0**.8 **V vs. Ag/AgCl**

under dark. The charge carrier density of bare BiVO4 and P-BiVO4 films was analyzed according to the below equation. " ? #?1 Nd ¼ eeoA2e 2 d c12 dV where Nd is donor density (in m?3), e is relative permittivity (68 for BiVO4 [16], eo is vacuum permittivity (=8.85 10-12F m?1), A is surface area (=2.83 10-5 m2 in this study), e is electronic charge (=1.602 10-19C), c is interfacial capacitance (in F), and V is applied voltage (in V).

5**The incident photon-to-current conversion efficiency (IPCE) was** obtained using **a**

Cornerstone 260 monochromator with a 300 W Xenon light source, based on the following equation. IPCEð%Þ ¼ 1240 Jphoto 100% Plight k where

8**k is the wavelength of monochromatic light** (in nm), Jphoto **is the** photocurrent **density** under **the light**

(in

30**mA cm?2**), and Plight **is the** measured irradiance **of the light**

(in mW cm?2). Charge separation and charge transfer efficiencies of the pho- toanodes were analyzed using hole scavenger sodium sulfite (Na2- SO3), assuming that the oxidation kinetics of sulfite ions by photogenerated holes is very fast and the charge transfer efficiency reaches 100% [17]. The charge separation (gseparation) and charge transfer (gtransfer) efficiencies were calculated by the following equation. g separation ¼ Jphoto;sulfite 100% Jabsorption gtransfer ¼ JJpphhoottoo;;swualftietre 100% where Jphoto,sulfite is the calculated photocurrent density by sub- tracting current density measured in 0.5 M Na2SO3 (pH 10.6) in dark from the current density obtained under irradiation, Jphoto,water is the calculated photocurrent density measured in 0.5 M Na2SO4, and Jabsorption is theoretical cumulative photocurrent density from light absorption, derived from integrating light absorptance with respect to AM 1.5G solar spectrum. 3. Results and discussion As depicted in Scheme 1, a controllable chemical treatment using sodium hypophosphite followed by coating NiOOH as cocat- alysts has been employed to modify BiVO4 films. The pristine BiVO4 films were first treated with 0.5 M hypophosphite (NaH2PO2) aque- ous solution to prepare hypophosphite-treated BiVO4 (labeled as P- BiVO4). Then, both BiVO4 and P-BiVO4 films were deposited with NiOOH cocatalysts using a pH-adjusting technique to get NiOOH--coated BiVO4 (NiOOH-BiVO4) and NiOOH-coated P-BiVO4 (NiOOH-P-BiVO4) [15]. The surface

27**morphology of** the **as- prepared photoanodes was investigated by scanning electron** microscopy. **As shown in**

Fig. 1a, the bare BiVO4 photoanode exhi- bits a nanoporous structure, in which BiVO4 nanoparticles aggre- gate in the nanoplate structures, which is in agreement with the reported literature [6a]. The SEM image of P-BiVO4 (Fig. 1b) reveals a highly similar structure, indicating that the post-synthetic treat- ment did not induce observable changes. Furthermore, the cocata- lyst modification of bare BiVO4 and P-BiVO4 photoanodes also exhibits little changes in morphology (Fig. 1c and d), probably owing to the characteristic of loading amorphous thin layer as cocatalysts [15]. XRD patterns have been collected to explore the influence of the post-treatment as well as loading NiOOH on the crystal structure of the photoanodes. As can be seen in Fig. 1e, all the diffraction peaks are attributed to the crystal facets of monoclinic scheelite BiVO4 (JCPDS no. 14–0688), except for the peaks annotated by asterisks which belong to the FTO substrate. The XRD patterns of these pho- toanodes are highly similar to each other due to the surface treat- ment and amorphous nature of the cocatalysts. Raman spectroscopy was then carried out to analyze possible structural changes induced by the post-treatment and the loading of NiOOH. As shown in Fig. 1f, the Raman bands located at 126, 211, 327, 367, 712, 827 cm?1 are all from the typical vibration modes of BiVO4 and no detectable changes in Raman shift can be observed among these photoanodes [18]. The features at 126 and 211 cm?1 are attributed to the crystal vibration modes of BiVO4. The bending modes of VO4 tetrahedra correspond to the peaks at 327 and 367 cm?1,

13**while the** shifts **at** 712 **and** 827 **cm?1 correspond to the** antisymmetric **and symmetric** stretching vibration **modes of the VO4**

tetrahedra, respectively [18c,19]. In addition, the

24**UV–vis**- ible **absorption spectra were** examined **to** explore **the** light absorp- tion **properties of** these photoanodes. **As shown in Fig**

. 1g, the BiVO4, P-BiVO4, NiOOH-BiVO4, and NiOOH-P-BiVO4 photoanodes exhibit similar absorption edges at around 510 nm. Besides, the calculated Tauc plots indicate that these photoanodes have a sim- ilar bandgap of approximately 2.44 eV, which is in agreement with the previous literature [1a,3a]. The as-prepared semiconductors Scheme 1. Preparation of NiOOH-P-

39**BiVO4 photoanodes. Fig**. 1. **SEM images of** the (**a) BiVO4, (b**) P-**BiVO4, (c**) NiOOH-**BiVO4, and (d**) NiOOH-P-**BiVO4**

photoanodes, and (e) XRD patterns, (f) Raman spectra, (g) UV–visible absorption spectra and (h) calculated Tauc plots of these photoanodes. still retained more than 95%

7**of the initial absorption after** 40 **days of exposure**. Due to **the**

fact that SEM images, XRD patterns, Raman spectra, and UV–visible spectra exhibit no noticeable differences among the BiVO4, P-BiVO4, NiOOH-BiVO4, and NiOOH-P-BiVO4 photoanodes, we infer that the bulk physical properties remain unchanged after the post-treatment and the loading of NiOOH cocatalysts. Therefore, efficacious techniques including transmission elec- tron microscopy, X-ray photoelectron spectroscopy, and electron paramagnetic resonance spectroscopy, have been employed to explore the morphological and structural alternations at the sur- face of these photoanodes. As shown in Figure S2a-c, no difference

4**can be observed** between **the** TEM images **of the BiVO4 and** P-**BiVO4** photoanodes, while the NiOOH-P-BiVO4 photoanode possesses an amorphous floccus-like structure at its surface which should be the loaded NiOOH cocatalysts. Besides, the SAED patterns reveal the single-crystalline nature of the BiVO4 nanoparticles (Figure S2- d-f). High-resolution TEM images were further collected, as pre- sented in Fig. 2. The lattice spacings

16**of the BiVO4**, P-**BiVO4, and** NiOOH-P-**BiVO4 photoanodes were**

determined to be 0.46

26**nm, 0**.31 **nm, and 0**.47 **nm, which** correspond **to**

(0 1 1), (?1 2 1), and (0 1 1) planes, respectively. Fig. 2a indicates that the bare BiVO4 photoanode has a relatively smooth surface. In contrast, it is wor- thy noted that a disordered atomic layer with a width of 2–3 nm has been created at the surface of the P-BiVO4 photoanode (yellow dash in Fig. 2b), which is related to the improved charge transfer property in BiVO4 [20]. The disordered surface layer can be pre- served after further loading thin overlayer of NiOOH (yellow dash in Fig. 2c). Apart from this, the

5**lattice spacing of 0**.243 **nm**, corre- sponding **to the** (1 **0** 1) **plane of**

nickel oxide hydroxide (JCPDS no. 06–0075), indicates that the formed cocatalysts are NiOOH instead of Ni(OH)2 or NiO. We also present another clearer TEM image of the NiOOH-P-BiVO4 photoanode in order to confirm the finding (Figure S3). The EDS spectrum reveals that surface elements are C, Cu, Bi, V, O, and Ni (Figure S4). The C signals may be induced by adventitious carbon contamination and the Cu signals are from the substrate, Cu mesh. Additionally, Fig. 2g shows the EDS map- ping results of the NiOOH-P-BiVO4 photoanode. Besides Bi, V and O, the element Ni can also be observed to uniformly exist at the surface of the photoanode. The weight and atomic proportion of the elements O, V, Ni, and Bi are listed in Table S2. Finally, it is explained that the semicircle structures shown in Fig. 2b (grey arrows) were induced by the electron-beam reduction process dur- ing TEM measurements. To explore the surface chemical characteristic of these photoan- odes,

10**X-ray photoelectron spectroscopy** technique **was carried out**. As shown **in** Figure S5, **the**

XPS full survey spectra indicate the exis- tence of Bi, V, and O in both BiVO4 and P-BiVO4 photoanodes. In addition to these elements, the signals of Ni have been detected in both NiOOH-BiVO4 and NiOOH-P-BiVO4 photoanodes. Fig. 3a shows the deconvoluted peaks for high-resolution O 1 s spectra of these photoanodes. The

14**O 1 s** spectra **can be fitted** into **three**

3**Fig. 2. High**-resolution TEM **images of** the (**a) BiVO4, (b**) P-**BiVO4, and (c**) NiOOH-P-**BiVO4** photoanodes, and (**d**

) EDS elemental mapping of the NiOOH-P-BiVO4 photoanode.

1**peaks at 529**.6 **eV, 530**.9 **eV, and** 531.8 **eV**, corresponding to **lattice oxygen (OL), oxygen** vacancy (Ovac), **and**

chemically absorbed oxy- gen (OC), respectively [12,21]. The

10**proportion of the** peak areas **is summarized in Table S1**

. It is noteworthy that the proportion of Ovac increases to 22% in the P-BiVO4 photoanode, 2-time

18**higher than that of bare BiVO4**, demonstrating **the** successful introduction **of** Ovac using **the**

hypophosphite treatment [1e]. In addition to the XPS analysis, we also employed electron paramagnetic resonance (EPR) spectroscopy to verify the generation of Ovac. As shown in Figure S6, the P-BiVO4 photoanode exhibits an apparent high EPR signal in comparison to the bare BiVO4. The EPR signal at g = 2.00 can be attributed to the Zeeman effect of single- electron-trapped Ovac [22]. The high signal of the P-BiVO4 photoan- ode indicates an improved level of Ovac, in line with the results of O 1 s deconvolution. In addition to the BiVO4 and P-BiVO4 photoan- odes, further overlaying NiOOH cocatalysts improves the amount of Ovac to 30% in the NiOOH-P-BiVO4 photoanode, compared to 26% in the NiOOH-BiVO4. The Bi 4f, V 2p, and Ni 2p high-resolution XPS spectra of these photoanodes have been examined as well (Fig. 3b-d). Compared with BiVO4, the P-BiVO4, NiOOH-BiVO4, and NiOOH-P-BiVO4 pho- toanodes exhibit

13**obvious low-energy** shifts **of Bi 4f and V 2p**

(red dash in Fig. 3b-c), revealing that the metal elements have been partially reduced, probably from Bi3+ to Bi2+ and from V5+ to V4+ [23]. In addition to the existence of Bi3+ (

21**4f7/2 and 4f5/2 peaks** located **at 158**.9 **eV and** 164.2 **eV), the**

deconvolution of Bi 4f spectra indicates that the P-BiVO4, NiOOH-BiVO4, and NiOOH-P- BiVO4 photoanodes also exhibit two other species of 4f7/2 (158.1 eV) and 4f5/2 (163.4 eV), which may be attributed to Bi2+ [1e,23c]. Similarly, the deconvoluting results of V 2p spectra also show the presence of V4+ in the P-BiVO4, NiOOH-BiVO4, and NiOOH-P-BiVO4 photoanodes (515.7 eV and 522.8 eV for V4+ 2p3/2 and V4+ 2p1/2, respectively), while all the photoanodes pos- sess the

26**peaks located at** 516.5 **eV and** 524.1 **eV**, which **are** ascribed **to** V5+ **2p3/2 and** V5+ **2p1/2**

spin–orbit splits, respectively [1e,23c]. The Ni high-resolution spectra were also characterized Fig. 3. High-resolution XPS spectra of (a) O 1 s, (b) Bi 4f, and (c) V 2p of the BiVO4, P-BiVO4, NiOOH-BiVO4, NiOOH-P-BiVO4 photoanodes, and (d) Ni 2p

11XPS spectra of the NiOOH-BiVO4 and NiOOH-P-BiVO4

photoanodes. to prove the formation of NiOOH with the pH-adjusting method.

13As shown in Fig. 3d, the fitted peaks located at 855.5 eV

(Ni2+ 2p3/2), 856.0 eV (Ni3+ 2p3/2), 873.2 eV (Ni2+ 2p1/2), and 875.7 eV (Ni3+ 2p1/2) illustrate the presence of Ni2+ and Ni3+, which is con- sistent with previous XPS results of Ni(OH)2 and NiOOH [15,24]. The satellite peaks can also be fitted as Sat 1, 2, 3, and 4 in the XPS deconvolution spectra To prove the effectiveness of sandwiching an Ovac interlayer between the bulk BiVO4 and the NiOOH overlayer, the

1photocurrent-potential (J-V) curves of the bare BiVO4, P-BiVO4, NiOOH-BiVO4, and NiOOH-P-BiVO4

photoanodes were conducted using a three-electrode configuration under AM 1.5G simulated sunlight (100 mW/cm2). As shown in Fig. 4a, the bare BiVO4 pho- toanode exhibits

4a low photocurrent density of 1.1 mA cm?2 at 1.23 V vs. RHE, which is comparable with

the values in previous studies [6a,25]. After the post-treatment, the P-BiVO4 photoanode reaches an improved photocurrent of 2.1 mA cm?2 at 1.23 V vs. RHE. By further coating NiOOH using the pH-adjusting method, a high photocurrent of 3.

42 mA cm?2 at 1.23 V vs. RHE in the NiOOH-P-BiVO4 photoanode is

obtained, in comparison to 2.3 mA cm?2 in the NiOOH-BiVO4. The onset potential of both BiVO4 and P-BiVO4 photoanodes reduces from around 0.80 V vs. RHE to 0.54 V vs. RHE. In addition to the J-V measurements, tran- sient amperometric measurements of these photoanodes were car- ried out

3at 1.23 V vs. RHE under chopped illumination

to evaluate charge recombination rate at the electrode||electrolyte junction (Fig. 4b). Among these photoanodes, the BiVO4 photoanode exhibits the sharpest photocurrent spike at the moment of light switch-on, indicating a considerable amount of charge carrier recombination. [26] After the hypophosphite treatment, the P- BiVO4 photoanode displays smaller spikes, suggesting the allevia- tion of charge carrier recombination. Moreover, the subsequent loading of NiOOH on both BiVO4 and P-BiVO4 photoanodes further reduces the probability of charge recombination by accelerating surface hole transfer [27]. The dark currents of as-synthesized semiconductors were almost no change after 10 days. The degrada- tions of PEC performance for those semiconductors were

7much slower (<5%) for the films stored under 0% RH and 50% RH after 35 days of exposure. In addition,

28**the applied bias photon-to- current efficiency (ABPE**), derived from the **J**-V **curves** [12], has been **employed to evaluate the PEC** efficiency **of these** modified BiVO4 **photoanodes**. As shown **in Fig**

. 4c, the bare BiVO4 photoan- ode exhibits a maximum ABPE value of 0.12% at 1.00 V, while an improved efficiency of 0.21% at 1.01 V for the P-BiVO4 photoanode is displayed. After loading NiOOH, the maximum ABPE values reach 0.43% and 0.66%

10**at 0**.88 **V vs. RHE for** NiOOH-**BiVO4** and NiOOH-P-**BiVO4**

photoanodes, respectively. To further investigate the photoresponsive properties of NiOOH-P-BiVO4 photoanode,

5**incident photon-to-current conversion efficiency (IPCE) as a** func- tion **of the** wavelength of monochromatic **light**

was performed

17**at 1.23 V vs. RHE (Fig**. 4d). **The IPCE values of the**

NiOOH-P-BiVO4 photoanode are 2.5–3.7

3**times higher than that of** the **bare BiVO4**, confirming **the** effectiveness **of**

Ovac as an interlayer between bulk BiVO4 and overlayer NiOOH. Fig. 4. (a) Photocurrent-potential (J-V) curves, (b) transient photocurrent response, (

31**c) applied bias photon-to-current efficiency (ABPE), and (d) incident photon-to-current conversion efficiency (IPCE) of**

the

11**BiVO4, P-BiVO4**, NiOOH-**BiVO4, and** NiOOH-**P-BiVO4 photoanodes**

. To further demonstrate the effectiveness of the additional Ovac interlayer, a 0.5 M sodium sulfite aqueous solution as hole scav- enger was used as an electrolyte for the J-V measurements. As shown in Figure S7a, all the photoanodes exhibit improved pho- tocurrents when measuring in the hole scavenger solution. It is noteworthy that the NiOOH-

3**BiVO4 photoanode** has **a** decreased **photocurrent density of** 4.42 **mA cm?2 at 1.23 V vs. RHE**

, in com- parison to 4.78 mA cm?2 in the bare BiVO4 photoanode, which may be

32**due to the recombination of electron-hole pairs** at **the**

BiVO4||NiOOH interface [6a,28]. By contrast, the P-BiVO4 photoan- ode

14**exhibits the highest photocurrent density of** 4.98 **mA cm?2 at 1.23 V vs. RHE, which**

may be attributed to the suppressed charge carrier recombination as a result of the surface Ovac interlayer. Because of the alleviated interfacial charge recombination, the photoresponse of the NiOOH-P-BiVO4 photoanode reaches 4.85 mA cm?2 at 1.23 V vs. RHE, compared to 4.42 mA cm?2 of the NiOOH-BiVO4. The cumulative photocurrent densities (Jabso- prtion) of these photoanodes were also collected. As shown in Fig- ure S7b, the

3**bare BiVO4**, P-**BiVO4**, NiOOH-**BiVO4, and** NiOOH-P- **BiVO4 photoanodes**

exhibit theoretical photocurrents of 5.53, 5.55, 5.58, and 5.60 mA cm?2, respectively, suggesting that all absorbed light energy is mostly converted into chemical energy. Based on experimental data, the charge separation (gsepartion) and charge transfer (gtransfer) efficiencies have been evaluated.

18**As shown in Fig**. 5a, **the** resulting **charge separation efficiency**

decreases from 86% in the BiVO4 to 77% in the NiOOH-BiVO4 photoanode at 1.23 V vs. RHE, revealing the occurrence of inter- facial charge recombination at the BiVO4||NiOOH interface [6a,28]. The introduction of the Ovac interlayer prior to loading NiOOH clearly enhances the charge separation efficiency from 77% in the NiOOH-BiVO4 to 85% in the NiOOH-P-BiVO4 photoan- ode. Moreover, surface hole transfer efficiency can also be enhanced with the post-treatment as well as the loading of NiOOH (Fig. 5b). Electrochemical impedance spectroscopy was further imple- mented to explore the surface charge transfer properties of these photoanodes [3a,5c]. The resultant EIS

27**data were fitted** with respect **to the equivalent circuit** model inserted **in**

Fig. 5c, and fit- ting parameters are shown in Table S3. In comparison to bare BiVO4, the reduced charge transfer resistance (Rct) in the P-BiVO4 and NiOOH-BiVO4 photoanodes indicates enhanced surface hole transfer. Interestingly, the NiOOH-P-BiVO4 photoanode exhibits an Rct of 795 X between that of P-BiVO4 (681 X) and NiOOH- BiVO4 (954 X), implying that the Ovac interlayer might not be com- pletely wrapped by the NiOOH overlayer, which is in agreement with the TEM observation. Moreover, the Mott-Schottky measure- ments were performed to estimate the charge carrier density in these photoanodes [1e,3b].

14**As shown in Fig**. 5d, **all the** photoan- odes **exhibit positive slopes**, revealing the **n-type**

semiconductor nature of the materials. The calculated donor densities are 4.91 10-26, 1.16 10-25, 4.95 10-26, and 9.72 10-26 m?3 for the BiVO4, P-BiVO4, NiOOH-BiVO4, and NiOOH-P-BiVO4 photoan- odes, respectively. It is evident that the donor density can be improved with the hypophosphite treatment but not the loading of NiOOH. The increased charge carrier density in the P-BiVO4 pho- toanode is probably due to the suppressed carrier recombination [1e]. The charge carrier recombination in these photoanodes has been evaluated by

40**photoluminescence (PL**) emission **spectra and time-resolved photoluminescence (TRPL) decay**

[29]. As shown in Figure S8a, all the photoanodes exhibit emission peaks at around 510 nm. The peak intensity decreases after the hypophosphite treatment and the loading of NiOOH, suggesting an overall sup- pression of charge recombination [29]. The TRPL technique was further utilized to explore the charge transport behavior in these

18**Fig. 5. (a) Charge separation efficiency** (gsepartion), (**b) charge transfer efficiency**

(gtransfer), (c)

11**electrochemical impedance** spectra (**EIS), and** (d) **Mott-Schottky** (M?S) **plots** of **the**

BiVO4, P-

2**BiVO4, NiOOH-BiVO4, and NiOOH**-P-**BiVO4** photoanodes. photoanodes. **The**

resultant TRPL curves were fitted using a tri- exponential decay function to estimate charge carrier lifetime (Fig- ure S8b). As shown in Table S4, compared to bare BiVO4 (9.02 ns), the increased average lifetimes in the P-BiVO4 (10.58 ns), NiOOH- BiVO4 (14.09 ns) and NiOOH-P-BiVO4 (14.84 ns), clearly indicates the reduced charge recombination rates. The chemical stability of the Ovac in photoelectrodes is of significance during the practical water splitting process. However, the stability mainly depends upon the processing approaches. For example, a previous study shows that argon-plasma-implantation generated Ovac has high stability over 40 h, owing to the increased active sites as well as optimized absorption and activation of water molecules [30]. By contrast, the argon-annealing process can also induce Ovac, but the Ovac-rich BiVO4 photoanode exhibits inferior stability, and the photocurrent density decreases from 1.1 mA cm?2 to 0.6 mA cm?2 [12]. In this work, 5-h amperometric measure- ments

8**were carried out to evaluate the stability of the** bare BiVO4, P-BiVO4, NiOOH-BiVO4, and the NiOOH-P-BiVO4 photoanodes.

35**As shown in Figure** S9, **the** bare BiVO4 photoanode **exhibits a** rapidly decreased **photocurrent** from **0**.7 **mA cm?2**

to 0.2 mA cm?2, revealing the photocorrsion of the BiVO4 photoanodes [2e,23c]. With the post-treatment, the photocurrent density of the P-BiVO4

1**decreases from 1**.8 **mA cm?2 to 0**.5 **mA cm?2**

, indicating the induced Ovac may not be stable during the water oxidation process. After loading a NiOOH layer, the stability of the NiOOH-P-BiVO4 photoanode exhibits a substantial improvement, from 3.2 mA cm?2 to 2.0 mA cm?2 during the process. The decreased photocurrent density may be due to the dropping of the amorphous floccus-like structure of the NiOOH layer during the 5-h tests [31]. Thus, further study on loading a uniform and thin layer as cocatalysts while preserving the generated Ovac layer may contribute to the performance and the stability of various photoelectrodes [12]. Ovac can be generated by a number of approaches including plasma/ion implantation [30,32], hydrogenation [33], post- annealing under inert atmosphere (e.g. Ar and N2) [34], reaction with reducing reagents [20a,c], electrochemical treatment [23], and elemental doping [35]. An inexpensive, effective, and facial hypophosphite treatment to induce Ovac in the BiVO4 photoanodes is presented in this work. The treatment alters the surface structure of these photoanodes but has little influence on the bulk characteristics, probably owing to the mild reduction activity of the chemical. It is reported that intrinsic Ovac can function to enhance charge mobility since two electrons released with the formation of one oxygen vacancy [36], which could be the reason for the enhanced charge carrier density, as indicated by the M?S measurement. Besides, the introduction of Ovac may tune the electronic structure of the BiVO4 photoanode, possibly resulting in the formation of an inter-band state [1e]. Such inter-band state has the chance to combine with the NiOOH overlayer to create a Helmholtz layer potential drop, which might be responsible for the suppression of interfacial recombination at the BiVO4||NiOOH junction [6a]. The charge transfer property of the P-BiVO4 is enhanced

4**in comparison to the bare BiVO4**, suggesting that **the**

generated Ovac might directly

4**participate in the water oxidation reaction**

[23c,30]. Despite this, the hypophosphite-induced Ovac did not lower the onset potential of the J-V curves. Further exploration on the structural and electronic structure of Ovac is of critical importance to determine how the Ovac, as surface states, to tune the energy level as well as to participating in the surface water oxidation reaction. 4. Conclusion In summary, a chemical treatment method has been utilized to create an Ovac interlayer at the surface of BiVO4 photoanode. The generated Ovac interlayer, sandwiched between the bulk BiVO4 and an OECNiOOH overlayer, can function to reduce interfacial charge recombination. Thereby, the rational construction of the BiVO4/Ovac/NiOOH structure improves charge separation and charge transport efficiencies, giving rise to the enhanced performance of PEC water oxidation. In addition, the chemical stability of the NiOOH-coated hypophosphite-treated BiVO4 photoanode is also improved, probably resulting from the reduced photocorrosion in the photoanode. The NiOOH cocatalyst can prevent the decrement of Ovac, while the Ovac interlayer serves as an inter-band state to reduce charge-carrier

recombination. This work demonstrates effective coordination between Ovac and cocatalysts, which paves a new route to develop efficient photo-responsive materials for practical applications in the field of

1**PEC water splitting. Declaration of Competing Interest The authors declare that they have no known competing** finan- cial **interests or personal relationships that could have appeared to influence the work reported in this paper. Acknowledgements The authors acknowledge financial support from the** Research Grants Council **of** Hong Kong (grant **no**

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16**Appendix A. Supplementary data Supplementary data to this article can be found online at https://doi.org/10.1016/j**.jcis.**2021**.10.063. **References**

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